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**RESEARCH ON LOW DENSITY THERMAL INSULATION MATERIALS FOR USE ABOVE 3000°F**

Seventh Quarterly Status Report

Contract NASr-99

National Beryllia Corporation

Haskell, New Jersey

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RESEARCH ON LOW-DENSITY
THERMAL INSULATION MATERIALS
FOR USE ABOVE 3000° F.

(NASA Contract NASr-99)
National Aeronautics and Space Administration
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Haskell, N. J.

## ABSTRACT

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Research and development on high-temperature thermal insulation materials is described with emphasis on the effect of internal radiation barriers and scattering agents on the thermal conductivity of Zirconia foams. A description is given of the technique for obtaining experimental thermal data at temperatures up to 4500° F under steady-state conditions. Curves of thermal conductivity versus temperature are presented for $ZrO_2$ foams containing dispersions of graphite and refractory metal particles and metal-coated ceramic microspheres. Author



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# INTRODUCTION

## 1.1 Purpose of the Program

Low-density foamed ceramic thermal insulation rapidly loses efficiency above 2400° F. due to the transfer of heat through the pores by thermal radiation. The purpose of this program is to study the reduction of this radiation or photon contribution to the thermal conductivity by the incorporation of a thermal radiation barrier phase into a low-density refractory structure. Mechanisms such as absorption and re-radiation by imbedded particles, scattering by incorporated phases and reflection by metallic foil radiation barriers are being investigated and evaluated.

## 1.2 Phases of the Program

The goals of this program are being achieved through the pursuit of the three phases described briefly below with details of the progress made during the seventh quarter discussed in Section II.

### Phase I. Technical Review

Review of previous high temperature heat transfer work essentially completed during the first quarter has been continued at a sufficient level of effort to keep abreast of the rapidly changing technology.

Phase II. Materials Formulation

The major effort of the program is concerned with the fabrication of low-density, low thermal conductivity materials. Light weight pure oxide ceramic matrices have been developed and impregnated with various volume percentages of potential radiation shielding phases introduced by a variety of techniques. Specimens of ceramic oxides whose thermal conductivity have been previously reported have also been prepared for calibration and equipment check-out purposes.

Phase III. Experimental Measurements

Evaluation of the thermal radiation barrier concept is being conducted in this phase of the program. A high temperature thermal conductivity test cell capable of maintaining under steady-state conditions specimen hot-face temperatures of 4500° F. has been fabricated and calibrated. Measurement of the apparent total conductivity of the ceramic foam composite test samples is in progress.

# DISCUSSION

## 2.1 Technical Review

A technical paper summarizing the research conducted under this contract was presented, by invitation, at the American Ceramic Society Southern Section Meeting in Birmingham, Alabama, December 5, 1963. At this time the Physical Property Measurements Laboratory of the Southern Research Institute was reviewed and technical discussions held with personnel making property measurements similar to those required in this program. These discussions and a close examination of experimental apparatus and techniques were helpful in correlating and evaluating minor differences in test results between the two laboratories.

Several reports on current research work presented at the 6th Refractory Composites Working Group Symposium, Fort Worth, Texas, January 10-12 were reviewed. One presented by the Marquardt Corporation (1) concerned the accuracy of temperature measurements by radiation and optical methods. A graph is included from which true temperature of a body may be determined from optical pyrometer and radiation pyrometer data. This method, very similar to one previously reported, (2) substantiates very closely the assumption of black body conditions within the sight holes of the present apparatus.

## 2.2 Materials Formulation

### 2.21 Carbon Systems

Specimens have been prepared containing five, ten, twenty and thirty percent by weight of graphite particles in a zirconia foam Zr28 type matrix. These specimens when sintered in an inert atmosphere to a time-temperature condition identical to the normal oxidizing firing cycle for the Zr28 type body, matured to significantly higher densities. Fabrication process changes were required in order to produce similar zirconia foam matrices in which the only difference was the presence or absence of the added graphite phase. The required specimen series may be fabricated during the next quarter.

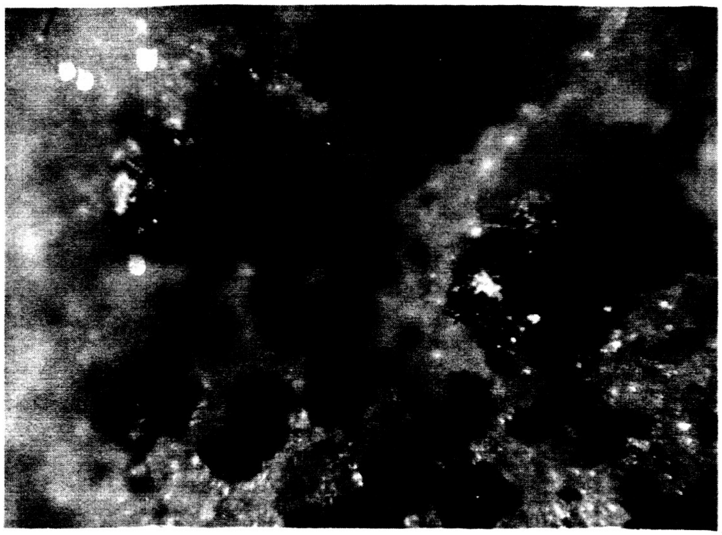
### 2.22 Metallic Tungsten Systems

Encouraging experimental evidence as discussed in Section 2.32 has prompted continued investigation into this composite system. As previously reported (3), zirconia foam Zr28 containing 5 and 10% by weight of a fine tungsten flake had been prepared for thermal conductivity measurement. Conductivity data from runs 24, 31, and 32 completed in this quarter, warranted a continuation of this series to 20 and 30% by weight tungsten flake and a duplication of previous specimens in order to confirm experimental results.

The specimen previously described (3) of foam Zr28 containing 10% by weight of tungsten-coated hollow zirconia microspheres was evaluated in runs 25 and 26 as reported herein. For comparison purposes a similar specimen also containing 10 weight percent of spheres but in this case not coated with tungsten was prepared and measured in run 29 and 30. Results were sufficiently encouraging so that a series of specimens containing 5, 10, and 20 weight percent of such coated and uncoated hollow zirconia microspheres are being prepared for subsequent evaluation. Figure 1 is a pair of photomicrographs at two different magnifications showing how these microspheres are incorporated into the zirconia foam matrix.

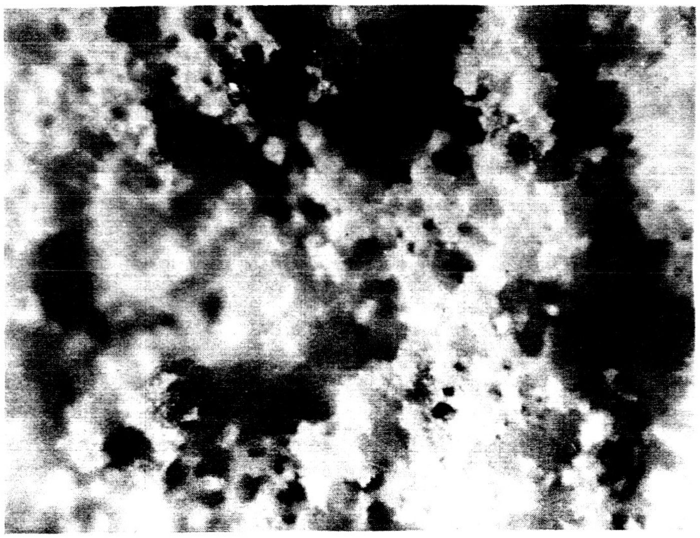
### 2.23 Molybdate Systems

Additional attempts using solution metallizing techniques have proven quite promising, especially compared with the discouraging results of the lithium molybdate-zirconia foam attempt in conductivity run #21. A fabricated, fired, and machined zirconia foam Zr28 matrix was impregnated in an ammonium molybdate solution, dried and fired in hydrogen to 2800$^{\circ}$ F. Optical examination and weight gain indicated a 10 weight percent surface absorption of discrete particles of molybdenum metal. A photomicrograph of this specimen is shown in Figure 2. Thermal conductivity data on this specimen measured in run #28, as shown in Figure 4, indicated a significant increase in insulation properties of this composite structure. A series of such specimens is being prepared which will be coated with 5, 10, 20 and 30% by weight of



⊢ 100 μ

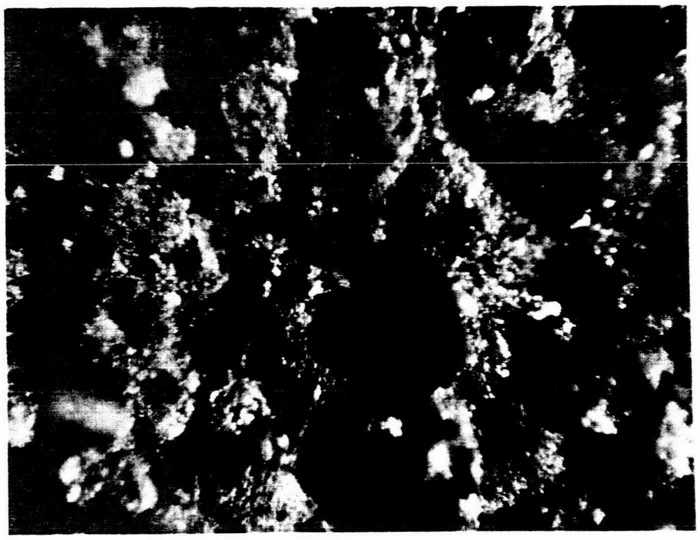
ZIRCONIA FOAM WITH TUNGSTEN COATED HOLLOW ZIRCONIA MICROSPHERES (50X)



⊢ 100 μ

ZIRCONIA FOAM WITH TUNGSTEN COATED HOLLOW ZIRCONIA MICROSPHERES (20X)

FIGURE 1



$\vdash\!\dashv$ 100 $\mu$

ZIRCONIA FOAM WITH MOLYBDENUM METAL PARTICULATE COATING BY SOLUTION METALLIZING TECHNIQUE (50X)

FIGURE 2

these discrete molybdenum particles. As further evidence of the effect of this solution metallizing technique a commercial bubbled alumina brick has been fabricated into thermal conductivity specimens and measured in run #27. Identical specimens have been impregnated using this solution metallizing technique and after drying and firing will be similarly measured. Data are incomplete.

### 2.24 Molybdenum Disilicide Systems

A series of specimens are being prepared containing molybdenum disilicide particles at percentage levels equivalent to those of the tungsten flake. This material which is oxidation resistant to over 3600° F. may prove to be a useful constituent of high temperature thermal insulation composites. Oxidation resistance is due to a surface formation of silicon dioxide. This oxide will react with zirconia to form zircon, (zirconium silicate), a refractory stable to 3600° F. The gross effect of this composite under present experimental conditions is yet to be evaluated.

## 2.3 Experimental Measurements

### 2.31 Thermal Transfer Cell Modifications

Figure 3 is a schematic sketch of the thermal conductivity test cell the way it is in current operation. It may be noted that all internal insulation has been removed with the exception of the molybdenum heat shields and the specimen itself. The terminal seal arrangement as shown is a water-cooled assembly electrically

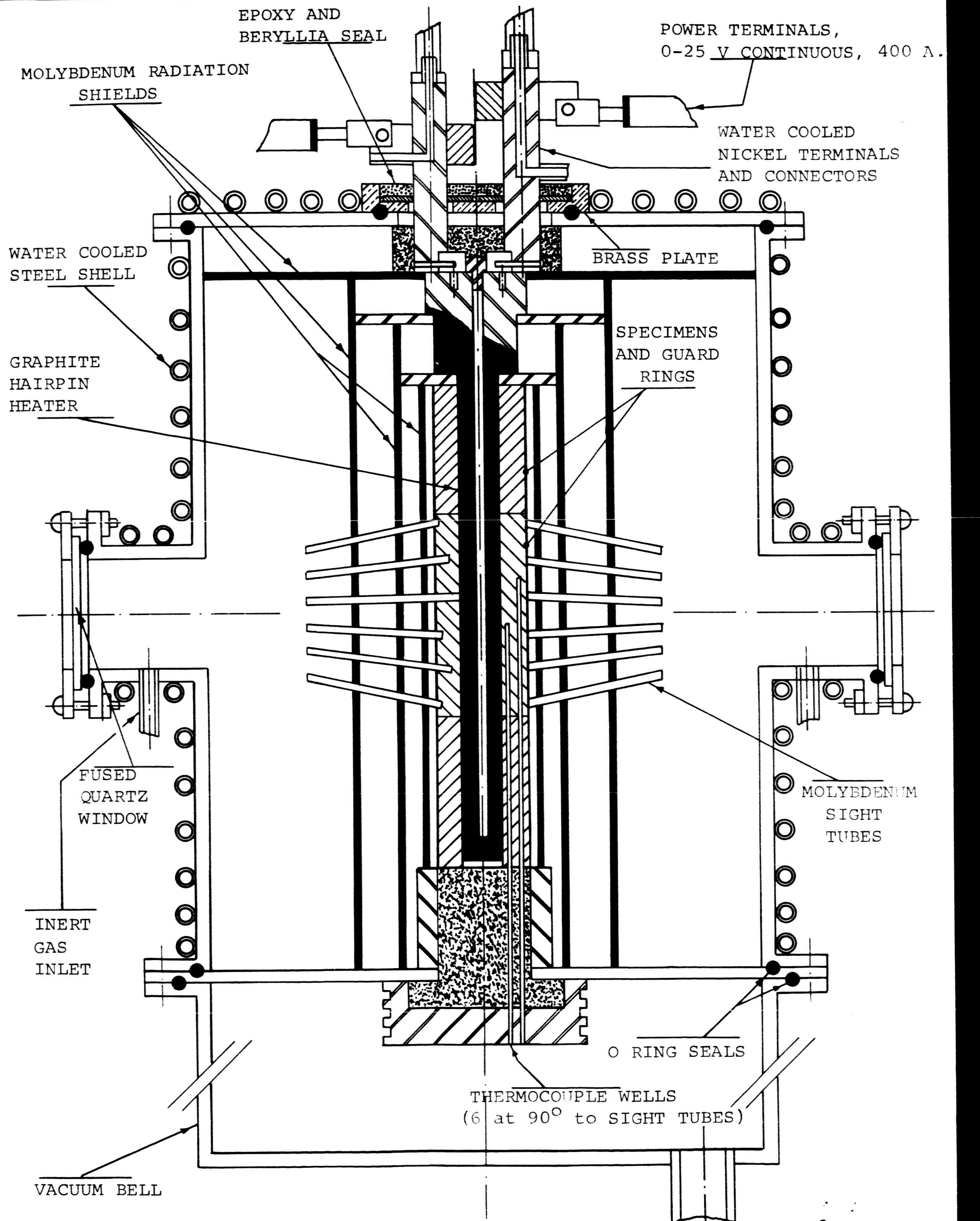

EPOXY AND BERYLLIA SEAL
POWER TERMINALS, 0-25 V CONTINUOUS, 400 A.
MOLYBDENUM RADIATION SHIELDS
WATER COOLED NICKEL TERMINALS AND CONNECTORS
WATER COOLED STEEL SHELL
BRASS PLATE
SPECIMENS AND GUARD RINGS
GRAPHITE HAIRPIN HEATER
FUSED QUARTZ WINDOW
MOLYBDENUM SIGHT TUBES
INERT GAS INLET
O RING SEALS
THERMOCOUPLE WELLS (6 at 90° to SIGHT TUBES)
VACUUM BELL

FIGURE 3

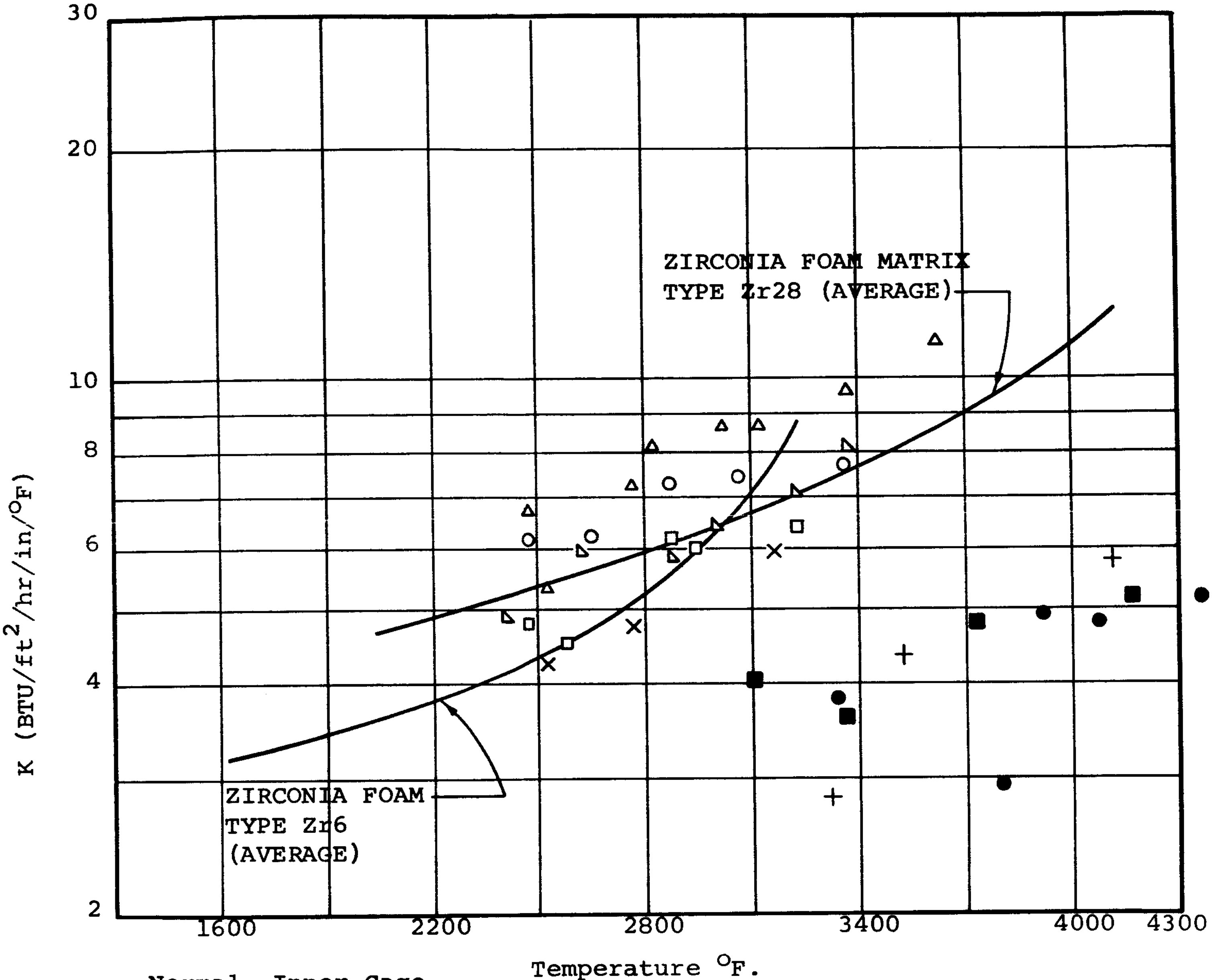
insulated and structurally supported by Berlox beryllia grit imbedded in an epoxy resin. This easily removable assembly is attached to the furnace shell simply by clamping against an O-Ring seal. In this manner the hair pin heater may be easily changed requiring only a few minutes of time. Since this modification, however, 11 runs have been made to temperatures as high as 4700° F. on the heater without any failure or need for element change. A vacuum bell used only occasionally in the past is also shown in Figure 3. This arrangement has been shown to be operative using only a 140 liter per minute roughing pump and liquid nitrogen cold trap to vacuums of 50 microns at 3000° F. heater temperatures. Vacuum is measured by a thermo-couple gauge at the top of the steel shell farthest away from the roughing pump port. A further modification of the experimental apparatus is the incorporation of a reactor in the primary of the AC power supply. This addition allows the 1 volt, step-wise transformer to be used continuously at any increment of voltage in the normal working range. Previously the number of thermal conductivity points in any particular run was limited by the steady-state conditions dictated by the increments of voltage available. This modification allows an infinite number of data points to be obtained.

As previously reported the hairpin design is limited in temperature due to the ionization of argon gas between the hairpin slot. This condition is exaggerated by poor thermal insulators because high power and therefore high voltage is required to produce high temperatures in a poorly insulating specimen assembly. Conversely, the ultimate temperature limit is increased when good thermal insulating materials are being tested. The specimen containing 20 weight percent of tungsten flake in run #32 achieved the highest temperature to date withstanding a steady-state condition for extended times at hot-face temperatures of 4450° F. This temperature was slowly increased to 4700° F. before conduction in ionized argon became a problem. It is apparent therefore, that the best thermal insulators available can be evaluated on this apparatus to hot face temperatures in excess of 4500° F.

### 2.32 Conductivity Measurements

Figure 4 is a thermal conductivity vs temperature plot for the specimens measured in runs 24 through 32. For comparison purposes average conductivity curves for zirconia foam matrix type Zr28 and Zr6 are included. Again the data reported are as measured and no attempt is made to correct or standardize these values with any thermal conductivity standards. Also no corrections are made for the several systematic sources of error possible with this comparative type apparatus.

It has been apparent that conductivity values measured in the inner gauge section, that is the 1/8 inch thick section adjacent




Normal Inner Gage

△ —— Run 24, Zr28 with 10% tungsten flake

○ ● —— Run 32, Zr28 with 20% tungsten flake

□ ■ —— Run 26, Zr28 with 10% tungsten coated spheres

◺ —— Run 30, Zr28 with 10% uncoated spheres

× + —— Run 28, Zr28 with 10% Moly $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$

FIGURE 4

THERMAL CONDUCTIVITY VERSUS TEMPERATURE

to the graphite hairpin heater, are significantly lower than data obtained from within the specimen. This is in part due to the measurement of heater temperature, rather than specimen hot face temperature when sighting down a "through" hole. In many of the measurements included in these data, however, the difference between these conductivity values has become more pronounced.

Typical of this effect are data from run 32, a Zr28 foamed zirconia containing 20% by weight (about 6% by volume) of fine tungsten flake. Normal gage section measurements, indicated by the open circles of Figure 4, show the total apparent thermal conductivity to be just slightly higher than a normal Zr28 foam. This would be expected in a low temperature range due to increases in overall density and the higher conductivity of tungsten compared with dense zirconia. Higher values even up to hot face temperatures of 3400$^{\circ}$ F. are not completely expected, however, seem more reasonable when it is remembered that the mean temperature of measurement is about 2500$^{\circ}$ F. Inner gage section measurements, indicated in Figure 4 by the closed circles show a marked drop to nearly half of that of the open circles. Indisputable evidence that this decrease in conductivity is real is the fact that observed heater temperature is substantially higher with the same power input than was recorded under identical conditions, except without a metallic phase present in the zirconia foam. Further, a heater temperature of 4700° F. the highest ever recorded, was obtained at a relatively small power input (1840 watts) before current by-pass through ionized argon occurred within the slot of the graphite hairpin heater. In several other runs on plain Zr28 specimens typical heater temperatures of 4300° F. were obtained at power inputs of 2860 watts.

The apparent break in this conductivity curve can be explained in part by the fact that at the same hot face temperature of 3400° F. in the inner gage section measurement, the mean temperature of measurement is about 2930° F. This does not, however, completely account for the break, nor does it justify plotting mean measurement temperature rather than maximum hot face temperature. Considerable studies of emmittance of the sight holes in the sample (still found by methods such as discussed in references 1 and 2 to approach unity), calibration of temperature measurement equipment and true sight hole determination by melting small strips of gold and platinum within sight holes, could not uncover measurement errors. Analysis of the specimen to determine if chemical change of the specimen materials, perhaps of the tungsten to tungsten carbide from heater vapors could account for this change are incomplete. No attempt has been made in Figure 4 to connect the raw data points from run 32. A smooth conductivity curve may only be drawn when sufficient evidence has been accumulated to replot the data in full light of all physical, chemical and thermal changes occuring within the specimen during measurement.

The open triangles of Figure 4 indicate that a 10 weight percent tungsten addition (about 3% by volume) merely increases thermal conductivity of the composite. This result is erroneous however, because this specimen, from run 24, conducted by a step-wise voltage increase, was badly thermal shocked and permitted much heat loss through failed sections. This surprisingly smooth curve is included to show how easily poor data may be mistaken for valid.

Very limited data (only three points in each gage section) were obtained on a fired Zr28 specimen which had subsequently been impregnated with ammonium molybdate solution, dried and reduced in hydrogen at 2800° F. These data are shown by the x and + (inner gage) points of run 28 in Figure 4. It is noteworthy that all comments made for the 20% tungsten flake of run 32 apply to run 28. A duplicate sample of this composition will be run using the continuously variable power supply to generate more data points.

An interesting comparison may be made between the data points of run 26 and 30. Both specimens were Zr28 type foam containing 10% by weight of hollow zirconia microspheres, about 200 microns in diameter. The spheres in sample 26, however, were coated with a 1 to 2 micron layer of tungsten metal by a vapor deposition technique. It may be seen in Figure 4 that the tungsten coated spheres only slightly lower the apparent thermal conductivity in the normal gage section (perhaps within experimental error) and that the inner gage section measurements from the tungsten containing specimen display the same dramatic reduction in apparent conductivity evident in runs 28 and 32. Discussion of these results will be delayed until analysis of samples is completed and replicate determinations confirm the validity of these results.

## CONCLUSIONS

Conductivity runs made during this quarter have shown the following:

1. The graphite hair-pin heater design is useful to much higher hot face temperatures in the testing of good thermal insulators than in the testing of poor ones. Maximum temperature obtained to date, without encountering current by-pass by conduction through ionized argon, is $4700^{\circ}$ F.
2. There is strong evidence that the metallic foil radiation barrier concept is effective in significantly reducing high temperature thermal conductivity.
3. A major discrepancy in thermal conductivity values calculated from inner gage section measurements, compared with measurements from more within the specimen material has been noted, particularly in samples containing metallic thermal radiation barrier phases. The reasons for this discrepancy has not yet been definitely established.

## PROGRAM FOR NEXT QUARTER

Fabrication and testing of Zirconia foam samples containing graphite, tungsten flake, tungsten coated hollow zirconia spheres, molybdenum particles by solution metallizing techniques and molybdenum disilicide will continue. Each type of thermal radiation barrier phase will be added in a series of concentrations in the approximate ranges 5 to 30% by volume.

A re-evaluation of thermal conductivity measurements made prior to run 30, the point where voltage adjustment was made continuously variable, will be made so that a greater number of points on the conductivity versus temperature curve may be obtained. Testing of a commercial bubbled alumina brick, with and without molybdenum impregnation, will be completed.

Major emphasis will be placed on determining the source of the discrepancy between inner gage section and normal gage section measurements, noted particularly in samples containing metallic foil radiation barrier phases.

1. Sklarew, S., "The Problem of Accurately Measuring Changing Temperatures of Non-Metallic Surfaces", The Marquardt Corp., presented at the Eighth Refractory Composite Working Group Meeting, Jan. 14-16, 1964.

2. Schwartz, H. S., "Laboratory Techniques for Studying Thermally Ablative Plastics", ASDTR61-517.

3. Styhr, K. H., "Research on Low Density Thermal Insulation Materials for Use above 3000° F.", Sixth Quarterly Status Report, NASr-99, October 1963.